The NOAA National Status and Trends Mussel Watch Program: National Monitoring of Chemical Contamination in the Coastal United States

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Abstract

Since 1986, the Mussel Watch Project within the NOAA National Status and Trends (NS&T) Program has been chemically analyzing sediments and molluscan tissues collected at sites throughout the coastal United States. Data from sediment analyses have been used to describe the status, or spatial distribution, of contamination on a national scale. The molluscan data, on the other hand, are used primarily to describe and follow temporal trends in contaminant concentrations. On the basis of accumulating knowledge on both the status and trends of chemical contamination, the NS&T Program has changed to some extent in terms of the chemicals it measures, its frequency of collection at individual sites, and its level of replication.

Introduction

The Mussel Watch Project within the National Status and Trends (NS&T) Program of the National Oceanic and Atmospheric Administration (NOAA) began in 1986 with the goal of determining the status and trends of chemical contamination in the coastal and estuarine United States. With that goal as a guiding principle, developing a program required making choices. Sites for sample collection had to comprise a set that could represent conditions the United States as a whole. The time scale for trends needed to be selected. Specific chemicals needed to be chosen. The matrices, or types of samples to be analyzed, had to reflect chemical concentrations at that site and time.

While all of these choices are to some extent arbitrary, the NS&T Program has annually measured concentrations of chemicals, that are mostly priority pollutants, in triplicate samples of sediment and in bivalve mollusks collected at fixed sites. As the program has evolved and reported on the spatial distribution of contamination and its temporal trends those initial choices are constantly reexamined. Chemicals have been added and subtracted, sites have been added, annual sampling continues for mollusks but not for sediment, and replicate samples are no longer collected. It is instructive to examine how the NS&T Program selected its sites and its chemicals, summarized its data in terms of status and trends, and adjusted its sampling strategy based on conclusions drawn from those analyses.

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Site Selection

The National Research Council recently reported (NRC, 1990) a need for large-scale, long-term monitoring in the coastal United States. The Council noted that more than $100 million is spent each year on compliance monitoring, i.e., testing wastewaters and other materials prior to discharge, or making measurements near discharge points as prescribed by regulation. Since compliance monitoring covers very small spatial scales, national programs such as the NS&T Program are needed to focus on wider scales. It is on this wider scale that national benefits should be derived from expending billions of dollars on regulating discharges of chemical contaminants. Because the Mussel Watch Project is designed to describe chemical distributions over these national and regional scales, its sampling sites need to be representative of rather large areas. To this end, no sites were knowingly selected near waste discharge points or poorly flushed industrialized waterways. Similarly, to avoid extremely local contamination, the program avoids collecting mollusks from artificial substrates such as pilings which are often chemically treated to inhibit decay.

A further requirement of the Mussel Watch Project is that indigenous mussels or oysters be collected for analysis. Mollusks can be put into cages to monitor chemical concentrations at any particular spot, and caging is done, for example, to monitor contamination near waste discharges (Martin, 1985) or during at-sea disposal of dredged material (Arimoto and Feng, 1983). For practical purposes, though, a program visiting sites throughout the nation must rely on natural populations being available at the time of annual sampling. So Mussel Watch sites can only be located where indigenous populations of mussels or oysters exist.

Lastly, the NS&T Mussel Watch Project is not the first use of mussels on a national scale for chemical monitoring in the coastal United States. In particular, Goldberg et al. (1983) sampled about 100 sites each year between 1976 and 1978. To allow comparisons of data with that program, its sites, when possible, were incorporated into the NS&T Program.

Mussel Watch sampling sites are not uniformly distributed along the coast. Within estuaries and embayments, they average about 20 kilometers (km) apart, while along open coastlines the average separation is 70 km. Almost half of the sites were selected in waters near urban areas, within 20 km of population centers in excess of 100,000 people. This choice was based on the assumptions that chemical contamination is higher, more likely to cause biological effects, and more spatially variable in these waters than in rural areas.

In 1986,145 Mussel Watch sites were sampled. In 1988 a few sites were added on the East Coast to fill in large spatial gaps between sites, and twenty new sites were selected in the Gulf of Mexico for the specific purpose of gathering samples closer to urban centers. Results from the initial sampling showed that the highest chemical concentrations were near urban areas on the East and West Coasts, and that few sites in the Gulf of Mexico could be considered

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contaminated. Since urban centers along the Gulf are further inland than those on other coasts, an attempt was made to sample further inland. The major limitation on doing that, however, is that oysters are not found at salinities below about 10 parts per thousand. By 1990, 234 sites had been sampled, with further additions made to test the representativeness of earlier sites.

Chemical selection

The elements and compounds measured in the NS&T Program are listed on Table 1. Not listed are Si, which is measured in sediment but not mollusks, and Sb and Tl which were not detected in mollusks during the first two years year of the program and are no longer measured. Except for Al, Fe, and Mn, the elements in Table 1 are all possible contaminants in the sense that their concentrations in the environment have been altered by human activities (Nriagu, 1989). The mere existence of the chlorinated organic compounds and butyltins is due to human actions. Polycyclic aromatic hydrocarbons are similar to metals in the sense that they occur naturally. They are found in fossil fuels such as coal and oil and are produced during combustion of organic matter. Their environmental presence, however, is also attributable to humans because they are released in the use and transportation of petroleum products and a multitude of human activities, from coal and wood burning to waste incineration create PAH compounds in excess of those that exist naturally.

Almost all the chemicals in Table 1 are also on list of 127 Priority Pollutants created by the United States Environmental Protection Agency in the late 1970's. Priority pollutants are chemicals which commonly appeared in discharged wastewaters and for which there were existing stocks of chemicals with which to make standard solutions (Keith and Teillard, 1979). Some of the alkylated PAH compounds and the butyltins in Table 1 are not Priority Pollutants because standards did not exist or the environmental occurrence of the compound was not recognized in the late 1970's.

The 74 priority pollutants that are not being measured are almost all low molecular weight, highly soluble, volatile organics. While they can be toxic they have relatively low tendency to leave the aqueous phase and be accumulated in organisms or on surfaces of sediment. Gossett et al (1983) measured concentrations of priority pollutants in effluent from a large sewage treatment plant and in organisms an sediments collected near the end of the discharge pipe. Compounds with low octanol-water coefficients (i.e. those with a relatively strong tendency to remain dissolved in water) were usually not detected or were in very low concentrations in organisms and sediments. In general, organic compounds monitored by NS&T have octanol-water coefficients greater than about 5000.

There are four priority pollutants that qualify for inclusion on the NS&T list of measured chemicals but are not measured; diethylhexylphthalate (DEHP), pentachlorophenol, endosulfan, and toxaphene. The latter two are pesticides, pentachlorophenol is a commonly used biocide, and DEHP is the most widely produced of the phthalates used extensively as plasticizers and, unlike other

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phthalates, resists degradation (Shelton et a., 1984) They are all compounds with high octanol-water coefficients and could be expected to be found in organisms and tissues. They have not been included among the NS&T chemicals because each requires special handling. All the organic analytes in Table 1, save butyltins, are extracted together from sediments or tissues. One aliquot of that extract is analyzed by GC-ECD (gas chromatography-electron capture detection) for the chlorinated compounds and GC-MS (gas chromatography-mass spectroscopy) for the polycyclic aromatic hydrocarbons. Measuring toxaphene requires a separate clean-up of that extract to remove the PCBs. One form of endosulfan (endosulfan sulfate) and pentachlorophenol require an entirely separate extraction procedure. Phthalate analysis is hindered by the ubiquitous presence of phthalates in all the plastic components of a laboratory. If DEHP were added to the NS&T list, special precautions, including isolation from the main analytical laboratory, would be required.

A third category of possible compounds are contemporary pesticides. Except for endosulfan, all the chlorinated pesticides and PCBs on the Priority Pollutant list and all those measured by NS&T are banned for use in the United States. We are monitoring what should be the gradual disappearance of these compounds as they disperse, or get buried in sediment, or very slowly decay. There are, however, many compounds that are registered for use on crops. Common herbicides are atrazine, alachlor, 2,4-D, and metalochlor, and common insecticides are carbaryl, carbforan, chlorpyrifos, and methyl parathion (Pait et al. 1992). Most contemporary pesticides share two common characteristics, either of which excludes them as possible candidates for annual monitoring. Generally they have low octanol-water coefficients so, when they are flushed from fields into natural waters they tend to stay dissolved rather than be accumulated by organism or adsorbed onto sediments. The few reports of the occurrence of contemporary pesticides in the environment (Goolsby et al, 1991, Holden et al, 1992, and the reports tabulated by Pait et al. 1992) all emphasize aqueous phase measurements. Secondly, the contemporary pesticides have relatively short half-lives. It is, of course, desirable that toxic chemicals break down rather than accumulate in the environment but that also makes it difficult to monitor such compounds unless sampling is done near the time of application.

In 1988 the NS&T Mussel Watch project did attempt to measure atrazine, alachlor, propanil, methyl parathion, and carbaryl in oysters from at two sites in the Maryland portion Cheasapeake Bay and one site in Winyah Bay, South Carolina. These pesticides are in use in those regions but none were detected in oysters. The annual NS&T sampling occurs in winter. Conceivably, if the oysters had been collected in spring at the time when pesticides are applied, they might have been found in the oysters. However, just as NS&T sites are chosen to be representative of areas rather than isolated "hot spots", it would not be representative of Chesapeake Bay or Winyah Bay if results depended on collecting in conjunction with pesticide application.

One contemporary insecticide, chlorpyrifros, has been detected in sediments off Central America (Readman et al., 1992). This compound is unusual among

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modern pesticides because of its very high octanol-water coefficient of more than 100,000. It is used in the United States (Pait et al., 1992) and is a potential analyte for the NS&T Program.

Since mollusks are collected annually there is opportunity to expand the list of analytes at some sites in some years. As explained this was done for three rural sites in an attempt to monitor some contemporary pesticides. It was done as well for butyltins in 1987 and 1988. In that case tributyltin and its breakdown products dibutyltin and monobutyltin were found almost at all tested sites and analyses for butyltins is now regularly done at all sites. In this case we expect to monitor a decrease in butyltin resulting from a 1988 law banning their further use as an anti-fouling agent on boats less than 25 m in length. A third category of chemicals, radionuclides, have been measured at a few sites on a one-time basis (Vallette-Silver and Lauenstein, 1992). Here the objective was to gather a set of current values for fallout nuclides (Cs-137, Am-240, and Pu-239,240) to compare with values obtained by Goldberg et al. (1983) in the late 1970's.

Species selection

Mussels or oysters are sampled at each Mussel Watch site. They were chosen as sentinel species because they are sessile, hardy, and, unlike fish, have limited capacity for metabolizing rather than simply accumulating polycyclic aromatic hydrocarbons. For essentially the same reasons, other programs have collected or are collecting mollusks for chemical analysis. Data from these programs are to some extent comparable with those from the NS&T Program. An example of an earlier nationwide program is that of Goldberg et al. (1983) in the late 1970's. That program, itself, was preceded by one conducted by Butler (1973) that, from 1965 to 1973, measured pesticide concentrations in marine organisms including mussels and oysters. The state of California has been monitoring coastal waters through analyses of mollusks since 1977 (Martin, 1985). Among other countries systematically monitoring through analyses of mollusks are France (Claise, 1989), Hong Kong (Phillips and Yim, 1981), Korea (KORDI, 1990), and New Zealand (ARWB, 1990). The Intergovernmental Oceanographic Commission of the United Nations begun an International Mussel Watch Program in 1992 with the collection of samples in South and Central America (Tripp et al., 1992). Cantillo (1991) has compiled a bibliography of more than 1200 citations where authors report chemical concentrations in mussels and oysters.

To extend as much as possible the ability to compare among sites, the ideal species would be available in all coastal areas of the United States. There is no such species but bivalve mollusks are fairly cosmopolitan. In clockwise progression around the continental United States, the mussel *Mytilus edulis* is collected at all sites from Maine to Delaware Bay, the oyster *Crassostrea virginia* is collected from Delaware Bay south and through the Gulf of Mexico, on the West Coast the mussels *M. edulis* and *M. californianus* are gathered.

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At three sites in Long Island Sound both the oyster *C. virginica* and the mussel *M. edulis* have been collected. At one site at the mouth of the Columbia River the mussels *M. edulis* and *M. californianus* were both collected.

Comparisons between species at common sites (Table 2) show that the trace elements Ag, Cu, and Zn are enriched in oysters by more than a factor of 10 relative to mussels. Conversely, Cr and Pb are more than three times higher in mussels. For other elements and for organic compounds there is no strong species effect between mussels and oysters. There are no important differences for elements or organic compounds between the two species of mussels. (The 3-fold difference in ΣDDT at the Columbia River site is ignored because the concentrations were very low in both mussel species.) There is some recent discussion among malacologists over whether the West Coast organism called *M. edulis* is actually *M. galloprovincialis* in California and *M. trossulus* towards the north. In fact, the three mussels may be strains of a single *Mytilus* species (Seed, 1992). Given this uncertainty, the mussels collected the Columbia River site may have been *M. trossulus* or even *M. galloprovincialis* instead of *M. edulis*. However, the lack of concentration differences between two *Mytilus* species at that site has been taken to validate comparisons among all mussels collected in the program.

Expanding the geographic extent of the Mussel watch Project has required collecting other species. There have been sites in Hawaii since the program began and the species has been the oyster *Ostrea sandvicensis*. To obtain molluscan data from Puerto Rico the mangrove oyster *Crassostrea rhizophorae* was obtained. Zebra oysters, *Dreissena polymorpha* were collected at seven sites in the Great Lakes in 1991. At one site in the Florida Keys, the smooth-edged jewel box, *Chama sinuosa* was obtained. In all these cases it is probably valid to compare concentrations of organic compounds with those from sites in the continental United States but the trace element concentrations may be species specific.

Sampling strategy

Mollusks are collected annually and in the winter (November through March) with each site occupied within 30 days of an annual target date. This timing is due to several reasons. Annual differences are the temporal scale of the program. Any season, so long as it was consistently used, would serve the objective of being annual. However, since mollusks may change their contaminant concentrations either by losing contaminants or losing biomass during the spawning process (Phillips, 1980), and since spawning usually occurs in spring and summer, it was considered prudent to sample in winter prior to spawning.

Every chemical analysis performed on mollusks is performed on composite samples of whole soft-parts of 20 oysters or 30 mussels. Separate composites are collected for inorganic and organic analyses. From 1986 through 1991, three separate composites were collected at each site in each year. So, for example, if a site was sampled every year from 1986 through 1990, the NS&T

data base would contain 15 values for the concentration of each chemical (three per year for five years). Multiple samples yield estimates of the variance of annual means at each site and it remains the NS&T practice to collect three composites if a site is being sampled for the first time. However, because estimates of annual variance are not used in analyses of trends, in 1992 the NS&T Program began collecting a single composite at annually sampled sites.

Sediment collections were made at every Mussel Watch site in 1986 and 1987. Since mussels or oysters are often found on hard bottom substrates such as rocks or shells, it was usually not possible to collect sediment at exactly the same location as mollusks. The protocol in 1986 was to collect three separate samples of the upper 2 cm of sediment at separate sites all within 500 m of the mollusk collection. Since 1987, the distance between sediment sampling stations has remained at 500 m but, in order to improve the ability to collect of muddy rather than sandy samples, the center of the sediment sampling site can be as far as 2 km from the mollusk site. Given the distances between sites and the national scale of the NS&T Program an offset of 2 km can generally be considered negligible

Since 1988 sediment collections have been made only at Mussel Watch sites not already sampled in prior years. This has been due to the fact that, in the absence of data on rates of sedimentation and biological mixing of sediment, the NS&T Program cannot know the time-scale represented by the upper 2 cm of sediment. For example, if mixing and deposition rates at a site are such that the upper 2 cm of sediment is a mixture of particles deposited over the prior ten years, sediment collections in consecutive years would essentially be annual collections of the same sample.

Since NS&T is designed to detect annual trends, chemical concentrations in one year have to be independent of those from other years. This independence does not exist for surface sediment samples, but there are data demonstrating that chemical concentrations in mollusks can reach altered steady-state concentrations over time scales of a few months or less, if concentrations change in the surrounding water or the food they filter from that water. Roesijadi et al. (1984) showed that when mussels were moved from a clean to a contaminated location in Puget Sound and vice-versa, concentrations of trace elements increased in the formerly clean mussels and decreased in the mussels moved to the clean location. In a similar reciprocal transplant experiment, Sericano et al. (1992) found PCBs, DDT, and PAH compounds to increase or decrease in response to their surroundings. Pruell et al. (1987) are among the many investigators to have shown that, under laboratory conditions, mussels accumulate or depurate contaminants as their exposure to chemicals is altered.

Analysis of status

The status of chemical contamination is its geographic distribution and trends are its temporal change. To document status, the NS&T Program has relied on data from analyses of sediment. All reports on status (NOAA, 1988, O'Connor

and Ehler, 1991, O'Connor, 1991, and NOAA, 1991) are, essentially, comparisons among sites and have all emphasized sediment data over that from analyses of organisms. This is simply due to the strong species-effect that for some elements precludes valid comparisons of molluscan data between sites with mussels and those with oysters.

While there is no species-effect on sediment concentrations, chemical concentrations do vary with sediment grain-size and it is not appropriate to compare concentrations measured in sandy sediments with those found in mud. If comparisons ignored the effect of grain-size, sites with sandier sediments would invariably appear the least contaminated. Sites receiving a relatively large amount of chemical contamination could go unrecognized simply because the sediments at that site were sandy and were, therefore, incapable of accumulating contamination.

The NS&T approach to the grain-size effect has been to simply divide all concentrations by the fraction of sediment in the sample that was silt or clay (i.e. the fine-fraction, particles < 63 μ in diameter). This adjustment, in effect, assumes that no chemical contamination is associated with sand and that sand in the sample was only diluting the contaminant concentration. If the fine-fraction was less than 0.2, meaning that more than 80% of the sample consisted of particles > 63 μ, the sample was not used for comparative purposes. That sample was not part of the calculated mean for the site. This treatment of the mostly sand samples excluded the mathematical possibility an adjusted concentration could be unrealistically high only because a low raw concentration was divided by a small fraction.

There was a premium, therefore, in finding muddy sediment samples with which to compare among sites. It has already been mentioned that a search for muddy sediments could extend up to 2 km from a Mussel Watch site. Nevertheless, of the 216 Mussel Watch Sites sampled between 1986 and 1989, 45 of them yielded only sand in every sample. That left data from 171 sites with which to make comparisons. Since there was no information on sediment deposition or mixing rates, it was assumed that all sediment data were temporally equivalent.   So all non-sandy sample data, regardless of year, from each site were used to determine mean concentrations for that site.

These data were augmented by data from 62 sites sampled by the NS&T Benthic Surveillance Project between 1984 and 1986. This project, through 1986, was similar to the Mussel Watch Project in the sense that it sampled surface sediment, while fish livers were analyzed rather than whole soft-parts of mollusks. The Benthic Surveillance Project differs from the Mussel Watch Project in that it has a component that seeks evidence of biological responses to contamination among the collected fish. This search for biological effects has, since 1987, forced the Benthic Surveillance Project to sample in areas of extreme contamination. These include the small scale patches of contamination near outfalls or in industrial waterways that are not considered representative of a general area.

The Benthic Surveillance data through 1986 and the Mussel Watch data through 1989 have been combined to form a set of sediment data on chemical contamination throughout the coastal and estuarine United States. The overall concentration distributions for each contaminant are approximately lognormal, and "high" concentrations were defined as those exceeding the mean plus one standard deviation of the lognormal distribution. Those "high" concentrations are useful for comparisons within the NS&T data set and with other reports on sediment contamination. The "high" concentrations in units of μg/g of dry fine-grained sediment for each contaminant are (in parentheses): Ag (1.2), As (24), Cd (1.2), Cr (230), Cu (84), Hg (0.49), Pb (89), Sn (8.5), Zn (270), ∑PAH (3.9),∑DDT (0.037), and ∑PCB (0.20).

Most of the high concentrations for any particular contaminant were found at sites near the urban areas of Boston, New York, San Diego, Los Angeles, and Seattle. Reports on the NS&T results (NOAA, 1988, O'Connor and Ehler, 1991, O'Connor, 1991, and NOAA, 1991) always recognize that there are innumerable examples of extremely high concentrations that are missed by the Program because it samples only "representative" sites. Cantillo and O'Connor (1992) compared the NS&T sediment data with data on trace elements in sediments from throughout the world. They found that logarithmic cumulative distribution plots of NS&T and worldwide data had similar means and standard deviations but diverged at the extremes. The worldwide data containing lower low concentrations and higher high values. The offset at the low end was attributed to the worldwide data set containing concentrations in sandy sediments while such sediments were excluded from the NS&T compilation. The high end of the worldwide data set contained concentrations from "hot spots", e.g. wastewater discharge ports or industrialized waterways. Such data are in the worldwide literature because it was usually gathered in the context of documenting particularly egregious environmental impacts. The NS&T Benthic Surveillance Project, for example, samples such locations with the specific purpose of testing for effects under extreme conditions.

Analysis of Trends

The effect of species on concentration limits the use of chemical concentrations in mollusks for defining the status of contamination. However, mollusk data are well-suited to analysis of trends. Here, the important parameter is the annual direction of change within a site. Species are irrelevant so long they remain constant at each site.

Temporal trends in molluscan concentrations have been sought through two non-parametric statistical tests on the data for 1986 through 1990 (O'Connor, 1992) One, the Sign test, is based on the fact that there are many sites with which to examine year-to-year changes. The other, Spearman rank correlation, examines the correlation between the ranks of concentration and year. Ranks, rather than actual concentrations, are used because one or a few unusually high or low concentrations near the beginning or end of a sequence can yield a significantly high parametric correlation, when in fact, there is no consistent pattern to the year-to-year changes. The Spearman test is sensitive only to the

direction of change rather than its size, its statistical strength is limited by the number of years for which there are data. With only five years of data, the "n" in the test is five and, to be significant at the 95% level of confidence, correlations coefficients must be at least 0.9. This means that only very strong, almost monotonic, trends could be detected.

The most common observation from the first five years of NS&T Mussel Watch data was that of no statistical change between years on a national scale and no strong trends in concentrations at individual sites. However, where the Sign test did find differences between the two years 1986 and 1990 they were only decreases. There were significant Spearman correlations between concentration and year in 13% of the site/chemical combinations and, among those, decreases were twice as frequent as increases. The overall conclusion was that levels of contamination in the coastal United States are decreasing.

That initial trend analyses was limited to the 141 Mussel Watch sites that were sampled annually over the first five years. Over that period, however, 233 sites had been visited. Four of the original sites were not sampled in two of the next five years because mussels or oysters were not available. Fifty five sites were added to the Program in 1988,1989, or 1990 and will not be examined for trends until 1993 or later. There are 33 sites where mollusks were sampled only once or, perhaps, twice. These are sites where mollusks are no longer found or where sites were added to check on representativeness of unexpectedly low or high levels of contamination at regularly sampled sites.

There is now a grid of about 200 sites at which trends can be monitored through systematic collection and analysis of mollusks. It is not necessary to continue collecting samples at every site in every year. As time passes, it becomes progressively less important to have data for each year over the entire span of years. The bare minimum of years necessary to calculate a meaningful Spearman rank correlation with 95% confidence is four. Tests were run at year five and trends needed to be very strong to be found at all. If we were willing to wait nine years to make the first attempt at trend detection, and had sampled in alternate years, we would still have an "n" of five, would still have required a correlation coefficient of 0.9 and, still only strong trends would have been detected. If data were available for each year over nine years, weaker trends could be found because the correlation coefficient would only need to be 0.60. However, with five years in hand, and starting to sample in alternate years there would be an "n" of seven in the ninth year and a required correlation coefficient of 0.71. Identified trends would need to stronger than if data were available each year, but trends would still be fairly accessible. The difference between required correlation coefficients corresponding to annual and alternate-year sampling become progressively smaller as time passes. At 13 years, for example the coefficients for the two sampling frequencies are 0.6 and 0.48 and by year 21 they become 0.37 and 0.41.

There are valid technical and, obviously, economic reasons to sample in alternate years. On the other hand, there is value in continuing to sample all 200 sites. O'Connor (1992) tested 14 chemical concentrations at 141 sites with

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five years of data and found 253 correlation coefficients ≥ 0.9. Since the test was run on 1974 site/chemical combinations (141 x 14) and since a 95% level of confidence was accepted, there would be 99 (.05 x 1974) cases where the correlations were seemingly significant but were, in fact, random. Adding chemicals and sites will increase the number of random correlations since, by definition, they will always be 5% of the combinations. Identifying the real trends requires similar behavior at nearby sites. With the first five years of data O'Connor (1992) was able to distinguish trends in Long Island Sound, Delaware Bay, and Terrebonne Bay as real trends because the same chemicals showed the same trends at nearby sites. The advantage of maintaining a 200-site network is the ability to identify real trends on the basis of geographic proximity among statistically identified trends.

The Sign test says nothing about individual sites but if the number of sites is large, say 50 or more, it can determine the significance of the direction of change between any two years. This method has been applied to the NOAA Mussel Watch data and also used to compare the NOAA Mussel Watch data with that from the previous program (Goldberg et al.,1983) of the late 1970's (Lauenstein et al., 1990). In the recent data, for example, it was concluded that total butyltin concentrations in the coastal United States are decreasing because its concentration was higher in 1989 at 103 of the 149 sites sampled in both 1989 and 1990. By the Sign test, the random chance of finding 103 out of 149 changes in one direction is <<0.05. At 39 of the 50 sites where both the earlier and the NOAA Mussel Watch Programs sampled mollusks, the Pb concentrations were higher in the 1970's. This was taken as evidence that Pb has decreased and was attributed to the fact that between the earlier and more recent measurements use of leaded gasoline decreased dramatically as new cars in the United States required unleaded fuel. Application of the Sign test on a national scale does not require a 200 site network, but if sites are sampled in alternate years there will be only 100 sites per year. That is still more than needed for national assessments but provides sufficient samples to look at year-to-year changes separately along East, West, and Gulf of Mexico Coasts.

Other U.S. monitoring programs

Through the Estuaries component of its Environmental Monitoring and Assessment Program (EMAP-EC), the United States Environmental Protection Agency has been conducting coastal and estuarine monitoring since 1990 (EPA,1990). In that year EMAP-EC sampled in the Virginian Province, i.e Chesapeake Bay northwards to the tip of Cape Cod. In 1991 monitoring continued in that Province and began in the Louisianian Province, all the U. S. coast along the Gulf of Mexico save southern Florida. In future years other provinces are to be added until EMAP-EC covers the entire coastal United States. The part of EMAP-EC dealing with chemical contamination measures the same chemicals as NS&T in sediments but EMAP-EC differs from NS&T in a number of ways. Most importantly, EMAP-EC does not analyze mussels or oysters and EMAP-EC does not sample at fixed-sites. Site selection is a rigorously random procedure. In 1990, 136 sites were occupied in the Virginian Province. Assuming similar coverage in all six provinces of the coastal and

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coterminous United States, EMAP-EC when it is national could be annually analyzing sediments from about 800 sites. This is more than three times the number of sites for which the NS&T Program has data and, in addition to the previous discussion, is a reason for NS&T to emphasize analyses of mollusks. Joint NOAA/EPA assessments of coastal contamination are being developed using data from both programs.

Since its inception, the NOAA program has included a chemical quality assurance component. Central to it is an annual intercomparison exercise where all laboratories analyze common samples supplied by the U. S. National Institute of Standards and Technology for organic compounds and the Canadian National Research Council for trace elements. Since 1990, the cost of this program has been shared with EMAP-EC and all labs analyzing samples for both the NOAA and EPA programs are participating.

Beyond that, however, there are myriad monitoring programs in the United States being conducted by state or local agencies. Usually the sampling grids for these programs provide more spatial resolution than NS&T or EMAP-EC but over small spatial scales. The national programs serve the more local programs in two ways. First, there are points in space where the local and nation programs overlap. These provide a basis for extrapolating the local results to larger scales. Second, the annual intercomparison exercises are open to the state and local programs. So, while their data remain confidential, programs beyond NS&T and EMAP-EC can document how well they agree with all other participants in the intercomparison exercises.

Conclusion

Monitoring is a series of systematic measurements over time or space or both. The temporal component of the NS&T Program consists of annually collecting mussels or oysters at about 200 sites and analyzing them for the chemicals listed in Table 1. Results have been used to test whether or not the imposition of controls on chemical discharges has resulted in decreases in levels of environmental contamination.

While estimates of concentrations that cause biological effects are also essential, determinations of the spatial distribution, or status, of chemical contamination are needed to define the extent of contamination problems in the coastal United States. Molluscan data provide spatial information, but the need to collect mussels at some sites and oysters at others excludes comparing concentrations of trace elements whose concentrations are strongly affected by species. Sediment contamination, on the other hand, is free of biological influence, so surface sediments were used to determine the status of contamination. However, even here, not all sediments have an equal capacity for accumulating contamination and analytical results needed to be adjusted by the proportion of sediment particles in the fine-grain ($<63\ \mu$ in diameter) size range. Because the time scale represented by the upper 2 cm of a sediment column is unknown without site-specific knowledge on rates of deposition and bioturbation, sediment data cannot be used to monitor temporal trends and

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annual collections of surface sediment ceased in the second year of the NS&T Program.

Other important changes since the program began in 1986 have been the realizations that determining temporal trends does not require replicate analyses in any given year and that, as years go by, there is less need for sampling every year rather than less frequently, but nonetheless systematically. Trends are identified not just by correlations between concentrations and time at individual sites but by parallel behavior at nearby sites.

Lastly, the NS&T Program is not alone in monitoring chemical contamination in the coastal United States. Its emphasis is on the national scale. On large regional scales, the U.S. EPA EMAP-EC Program measures the same chemicals in sediments. Together NS&T and EMAP-EC sponsor an annual chemical quality assurance program that is open to organizations monitoring on state and local levels. Combining data from these programs increases the spatial resolution of the large scale undertakings such as NS&T and expands the perspective of the smaller scale efforts.

References

Arimoto, R. and S. Y. Feng. 1983. Changes in the levels of PCBs in *Mytilus edulis* associated with dredged-material disposal. pp. 199-212. In Kester, D. R. et al. (eds.) Wastes in the Ocean Vol. 2. Dredged-Material Disposal in the Ocean. Wiley and Sons, NY

Aukland Regional Water Board (ARWB). 1990. N.Z. Steel Limited Environmental Monitoring Program. Fourth Annual Report. Technical Publication 68. Aukland Regional Water Board , Aukland, New Zealand, 78 pp.

Butler, P. A. 1973. Residues in fish, wildlife, and estuaries. Pest. Monit. Bull. 6: 238-262

Cantillo, A. Y. 1991. Mussel Watch Worldwide Literature Survey-1991. NOAA Technical Memorandum NOS ORCA 63. 143 pp.

Cantillo, A. Y. and T. P. O'Connor. 1992. Trace Element Contaminants in Sediments from the NOAA National Status and Trends Program Compared to Data from Throughout the World. Chemistry and Ecology 7: 31-50

Claisse, D. 1989. Chemical contamination of French coasts: the results of a ten-year Mussel Watch. Mar. Pollut. Bull. 20: 523-528

Environmental Protection Agency (EPA). 1990. Environmental Monitoring and Assessment Program. Near Coastal Program Plan for 1990: Estuaries. U. S. Environmental,Protection Agency Report EPA/600/4-90/033, Washington DC 217 pp. & appendices

Goldberg, E.D., M. Koide, V. Hodge, A.R. Flegal, and J. Martin. 1983. U.S. Mussel Watch: 1977-1978 results on trace metals and radionuclides. Estuarine, Coastal and Shelf Sci. 16: 69-93.

Goolsby, D. A., R. C. Coupe, and D. J. Markovchik. 1991. Distribution of Selected Herbicides and Nitrate in the Mississippi River and its Major Tributaries, April through June 1991. Water-Resources Investigations Report 91-4163, U.S. Geological Survey, Denver, CO. 35 pp..

Gossett, R. W., D. A. Brown, and D. R. Young. 1983. Predicting the bioaccumulation of organic compounds in marine organisms using octanol/water partition coefficients. Mar. Pollut. Bull. 14: 387-392

Keith, L. H. and W. A. Teillard. 1979. Priority pollutants I: a perspective view. Environm. Sci. Technol. 13: 416-423

Korean Ocean Research and Development Institute (KORDI). 1990. A Study on the Coastal Water Pollution and Monitoring - Third Year. BSPG 00112-315-4, Korean Ocean Research and Development Institute, Seoul, Korea, 261 pp.

Source: pgs. 331-349 In: C. R. Cothern and N. P. Ross (eds.) Environmental Statistics, Assessment and Forcasting, Lewis Pub. Boca Raton, FL (1994)

Lauenstein, G. G., A. Robertson, and T. P. O'Connor. 1990. Comparisons of trace metal data in mussels and oysters from a Mussel Watch Program of the 1970's with those from a 1980's Program. Mar. Pollut. Bull. 21: 440-447

Martin, M. 1985. State Mussel Watch: Toxics surveillance in California. Mar. Pollut. Bull. 16: 140-146

National Research Council (NRC). 1990. Managing Troubled Waters; The Role of Marine Environmental Monitoring. National Academy Press, Washington, DC. 125 pp.

NOAA. 1991. Second Summary of Data on Chemical Contaminants in Sediments from the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 59. 29 pp. & appendices

Nriagu, J. O. 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338: 47-49

O'Connor, T. P. 1990. Coastal Environmental Quality in the United States, 1990. Chemical Contamination in Sediments and Tissues. A Special NOAA 20th Anniversary Report, NOAA Office of Ocean Resources Conservation and Assessment, Rockville, MD 34 pp.

O'Connor, T.P. and C. N. Ehler. 1991. Results from NOAA National Status and Trends Program on distributions and effects of chemical contamination in the coastal and estuarine United States. Environm. Monit. and Assess. 17: 33-49

O'Connor, T. P. 1992. Recent Trends in Coastal Environmental Quality: Results from the First Five Years of the Mussel Watch Project
NOAA Office of Ocean Resources Conservation and Assessment, Rockville, MD 29 pp. & appendices

Pait, A. S., A. E. DiSouza, and D. R. G. Farrow. 1992. Agricultural Pesticides in Coastal Areas: A National Summary. NOAA, National Ocean Service, Office of Ocean Resources Conservation and Assessment, Rockville, MD. 112 pp.

Pait, A. S., D. R. G. Farrow, J. E. Lowe, and P. A. Pacheco. 1989. Agricultural Pesticide Use in Estuarine Drainage Areas: A Preliminary Summary for Selected Pesticides. NOAA, National Ocean Service, Office of Ocean Resources Conservation and Assessment, Rockville, MD. 134 pp.

Phillips, D. J. H. 1980. Quantitative Aquatic Biological Indicators. Applied Science Publishers, London 488 pp.

Phillips, D. J. H., and W. W. S. Yim, 1981. A comparative evaluation of oysters, mussels, and sediments as indicators of trace metals in Hong Kong waters. Mar. Ecol. 6: 285-293

Pruell, R.J., J.G. Quinn, J.L. Lake, and W.R. Davis. 1987. Availability of PCBs and PAHs to *Mytilus edulis* from artificially resuspended sediments. pp. 97-108. In:

Source: pgs. 331-349 In: C. R. Cothern and N. P. Ross (eds.) Environmental Statistics, Assessment and Forcasting, Lewis Pub. Boca Raton, FL (1994)

Capuzzo, J.M. and D.R. Kester (eds.) Oceanic Processes in Marine Pollution. Vol. 1. Biological Processes and Wastes in the Ocean. Krieger, Malabar, FL.

Readman, J. W., L. Liong Wee Kong, L. D. Mee, J. Bartocci, G. Nilve., J. A. Rodriguez-Solano, and F. Gonzalez-Farias. 1992. Persistent organophosphorus pesticides in tropical marine environments. Mar. Pollut. Bull. 24: 398-402

Roesijadi, G., J.S. Young, A.S. Drum, and J.M. Gurtisen. 1987. Behavior of trace metals in *Mytilus edulis* during a reciprocal transplant field experiment. Mar. Ecol. Prog. Ser. 15: 155-170.

Sericano, J. L., T. L. Wade, and J. M. Brooks. 1992. The usefulness of transplanted oysters in biomonitoring studies. Proceedings of the Coastal Society Twelfth International Conference. (in press)

Shelton, D. R., S. A. Boyd, and J. M. Tiedje. 1984. Anaerobic biodegradation of phthalic acid esters in sludge. Environm. Sci. Technol. 18: 93-97

Tripp, B. W., J. W. Farrington, E. D. Goldberg, and J. Sericano. 1992. International Mussel Watch: the initial implementation phase. Mar. Pollut. Bull. 24: 371-373

Vallette-Silver, N. and G. G. Lauenstein 1992. Radionuclides in bivalves collected along the Coastal U. S.:Preliminary results. MTS '92. Marine Technology Society, Washington DC,

Table 1. Chemicals measured NOAA NS&T Program

DDT and its metabolites	Polycyclic aromatic hydrocarbons[b]	Major elements	
2,4'-DDD	2-ring	Al	Aluminum
4,4'-DDD	Biphenyl	Fe	Iron
2,4'-DDE	Naphthalene	Mn	Manganese
4,4'-DDE	1-Methylnaphthalene		
2,4'-DDT	2-Methylnaphthalene		
4,4'-DDT	2,6-Dimethylnaphthalene		
	1,6,7-Trimethylnaphthalene		
		Trace elements	
Chlorinated pesticides other than DDT	3-ring	As	Arsenic
	Fluorene	Cd	Cadmium
	Phenanthrene	Cr	Chromium
Aldrin	1-Methylphenanthrene	Cu	Copper
Cis-chlordane	Anthracene	Pb	Lead
Trans-nonachlor	Acenaphthene		
Dieldrin	Acenaphthylene	Hg	Mercury
Heptachlor		Ni	Nickel
Heptachlor epoxide	4-ring	Se	Selenium
Heptachlor	Fluoranthene	Ag	Silver
Heptachlor epoxide	Pyrene	Sn	Tin
Hexachlorobenzene	Benz(a)anthracene	Zn	Zinc
Lindane (gamma-BHC)	Chrysene		
Mirex			
	5-ring		
Polychlorinated biphenyls	Benzo(a)pyrene		
	Benzo(e)pyrene		
PCB congeners 8, 18, 28,	Perylene		
44, 56, 66, 101, 105, 118,	Dibenz(a,h)anthracene		
128, 138, 153, 179, 180,	Benzo(b)fluoranthene		
187, 195, 206, 209	Benzo(k)fluoranthene		
Tri- di-, and mono-butyltin	6-ring		
	Benzo(ghi)perylene		
	Indeno(1,2,3-cd)pyrene		

Table 2. Ratios of mean concentrations of trace elements and of aggregated groups of organic compounds measured in two species at the same sites in 1988 and 1989. Ratios are underlined if they ≥3.0 or ≤ 0.3

SITE[a]	Yr	species[b]	Ag	As	Cd	Cr	Cu	
CRSJ	88	mc/me		0.76	1.13	0.65	0.67	0.97
CRSJ	89	mc/me		.c	0.95	0.68	1.18	0.76
LIHR	88	cv/me		14.04	0.82	1.93	0.19	31.47
LIHR	89	cv/me		6.15	0.80	1.87	0.21	32.89
LINH	89	cv/me		4.87	0.85	2.21	0.21	17.11
LIPJ	89	cv/me		20.63	0.81	1.71	0.24	25.26

SITE	Yr	species	Hg	Ni	Pb	Se	Zn	
CRSJ	88	mc/me		0.52	1.09	0.84	0.92	0.90
CRSJ	89	mc/me		0.66	0.74	2.19	0.82	1.21
LIHR	88	cv/me		0.77	2.43	0.30	0.70	40.00
LIHR	89	cv/me		0.65	1.91	0.24	0.59	38.33
LINH	89	cv/me		0.66	0.89	0.24	.	28.71
LIPJ	89	cv/me		1.07	2.07	0.28	0.84	47.73

SITE	Yr	species	ΣCdane[d]	ΣDDT[d]	ΣPCB[d]	ΣPAH[d]
CRSJ	88	mc/me	1.22	0.27	0.53	1.04
CRSJ	89	mc/me	.	.	.	.
LIHR	88	cv/me	0.87	0.86	0.63	0.63
LIHR	89	cv/me	1.27	1.11	0.96	0.94
LINH	89	cv/me	1.01	0.95	0.98	0.89
LIPJ	89	cv/me	.	.	.	.

[a]Sites designated as CRSJ, LIHR, LINH, LIPJ are Columbia River South Jetty, Long Island Sound Housatonic River, Long Island Sound New Haven, and Long Island Sound Port Jefferson, respectively.

[b]Species designated as mc,me, and cv are *Mytilus californianus* , *M. edulis* and *Crassostrea virginia* , respectively.

[c]Ratios are missing (.), if the chemical was not detected in one or both species

[d]The aggregated groups of organic compounds are; ΣCdane= the sum of cis-chlordane and trans-nonachlor and two minor components, heptachlor and heptachlorepoxide. ΣDDT=sum of six compounds (o,p and p,p isomers of DDE, DDD, and DDT). ΣPCB=sum of 18 congeners, ΣPAH=sum of 20 polycyclic aromatic hydrocarbons.